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Boroaluminosilicate glasses serve as the basis for a variety of industrial glasses. Hence, it is critical to understand the relationship between physical properties and structure of these mixed network former glasses. Also it is important to model the effects of composition on properties based on structural speciation by applying constraint theory and then to compare the modeled and experimental results. We have designed six Na_2O-B_2O_3-Al_2O_3-SiO_2 glasses with variation of the $[Al_2O_3]/[SiO_2]$ ratio to access different regimes of sodium behavior. We use ^{11}B, ^{27}Al, ^{29}Si, and ^{23}Na MAS NMR to determine changes in both network speciation and modifier cation environment as a function of the composition. We link these structural changes to changes in measured thermal, mechanical, and rheological properties.